

Photochromic Smart Windows Employing WO₃-Based Composite Films

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Abstract

WO₃-based composite films were fabricated from peroxy-iso-poly tungstic acid and a transparent urethane resin, and the photochromic properties of the films were evaluated under sunlight from three seasons: spring, summer, and winter. All composite films exhibited photochromism under solar irradiation, and the coloring degree of the films varied with the sunlight intensity for each season. We estimate the energy efficiency of the colored composite films for various seasons.

Keywords: tungsten trioxide, composite, film, photochromism

1. Introduction

Several energy-efficient window materials have been investigated, including heat mirror materials (Granqvist, 2007; Shanthi et al., 1982; Jie, Xin-shi, & Xing-fang, 1998), thermochromic materials (Granqvist, 2007; Miyazaki & Yasui, 2006; Takahashi, Hibino, & Kudo, 1996), photochromic materials (Granqvist, 2007; Armistead & Stookey, 1964; Scarminio, Lourenco, & Gorenstein, 1997; Miyazaki et al., 2013), and so on (Miyazaki et al., 2011; Miyazaki et al., 2013). The photochromic properties of WO₃-based materials result from the reduction of W⁶⁺ to W⁵⁺ in the WO₃ host upon UV irradiation (Miyazaki et al., 2011; Miyazaki et al., 2012; Miyazaki et al., 2014; Miyazaki et al., 2015). Using WO₃-based photochromic materials, the level of sunlight transmitted through the window can be controlled. The WO₃ based films show high transmittance at the bleached condition and shows considerable low transmittance at the colored condition (Miyazaki et al., 2011; Miyazaki et al., 2012; Miyazaki et al., 2014; Miyazaki et al., 2015). Therefore, the change in transmittance according to the intensity change of sunlight is large, and it is expected as a smart window.

In previous studies, we fabricated photochromic composite films comprising dispersed WO₃ nanoparticles using peroxy-iso-poly tungstic acid (W-IPA) and a transparent urethane resin. The photochromic properties of the composite films were improved by adding other elements or controlling the atmosphere around the composite films (Miyazaki et al., 2011; Miyazaki et al., 2012; Miyazaki et al., 2014; Miyazaki et al., 2015). The films showed reversible photochromic properties under UV irradiation provided by a Hg lamp, but the photochromic properties of the composite films have not yet been evaluated under sunlight irradiation.

In the present investigation, the photochromic properties of WO₃-based composite films were evaluated under sunlight from various seasons for application as practical smart windows. Furthermore, the energy efficiency of the WO₃-based composite films was calculated from their coloration properties.

2. Experimental Procedure

The preparation of W-IPA and the composite films has been previously described (Miyazaki et al., 2011; Miyazaki et al., 2012; Miyazaki et al., 2014; Miyazaki et al., 2015). W-IPA was prepared via a direct reaction of tungsten metal and hydrogen peroxide. The resulting W-IPA powder was dissolved in methanol at a concentration of 0.1 mol/L, and 0.2 mL of the solution was mixed with 3.2 g (3 cm³) of liquid-type urethane resin (M-40; Asahi Kasei Chemicals Corp., Japan). The liquid urethane resin was then cured via UV-Vis light irradiation. The precursor mixture (in a slurry state) was degassed at 1 kPa for 60 min to remove dissolved air. Subsequently, the precursor slurry was placed between glass slide with the thickness of 1300 μm. The precursor was cured by UV irradiation, and the resulting composite films were removed from the glass slide substrates.

The photochromic properties of the composite films were measured with a UV–Vis spectrophotometer (UV-1600; Shimadzu Corp., Japan), and coloring of the composite films was carried out under natural sunlight. We chose measurement days close to the vernal equinox day (14th April in 2014, Date A), summer solstice (15th July in 2014, Date B) and winter solstice (2nd December in 2015, Date C). The weather conditions on these days are shown in Table 1 (Japan Meteorological Agency, n.d.); the cloud cover on these days was less than 10%. Sunlight irradiation of the composite films was undertaken for various durations starting at 10:00 AM on each day. From the radiant intensity of the sunlight at each day and transmittance spectra of the composite films, energy saving ratios of sunlight through the composite films were evaluated in the wavelength range of 200–1100 nm.

Table 1. Weather conditions on each date.

Date	Irradiance (W/m ²)	Temperature (°C)	Cloud cover (%)
Date A (14 th Apr. 2014)	710	16.0	0
Date B (15 th Jul. 2014)	921	30.2	4
Date C (2 nd Dec. 2015)	413	16.8	10

3. Results and Discussion

The photochromic properties of the composite films were evaluated by sunlight irradiation on the aforementioned dates. Figure 1 shows the UV–Vis transmittance spectra of the composite films before and after sunlight irradiation. Figure 2 depicts an overview of the composite films before and after sunlight irradiation. All colored films showed broad absorption with peaks at around 650 and 900 nm, and the results agreed well with previous investigations (Miyazaki et al., 2011; Miyazaki et al., 2012; Miyazaki et al., 2014; Miyazaki et al., 2015). The coloring degree of the composite films depends on the date. The composite films were most colored in the summer and least colored in the winter. These results are consistent with the captured images of the films and suggest that the coloring degree of the films depends on the sunlight intensity, which varies depending on the season. All composite films became bleached in a dark room, and the reversible photochromic properties of the films agreed with previous reports (Miyazaki et al., 2011; Miyazaki et al., 2012; Miyazaki et al., 2014; Miyazaki et al., 2015).

Figure 3 illustrates the time dependences of transmittance changes at 650 nm during coloring and bleaching for all composite films. For films measured on dates A (spring) and B (summer), although the coloring degree had not fully saturated after 1 h of sunlight irradiation, the films were sufficiently colored. On the contrary, the coloring degree of the film measured on date C (winter) was saturated after 1 h of sunlight irradiation. In general, the coloring speed changes with the ambient temperature. The difference in temperature between dates A, B, and C was at most 10 °C; thus, the coloring degree of all films is assumed to depend on the sunlight radiant intensity, with only a weak dependence on ambient temperature. All colored films took 20–30 h to bleach back to their initial state.

Using a solar reference spectrum (Solar Spectra, n.d.) and the spectra of the colored films after solar irradiation for 1 h (Figure 1), we calculated the solar energy spectra transmitted through the colored composite films, as shown in Figure 4. Since the absolute solar irradiance on the surface changed with the season, we employed an arbitrary unit for the vertical axis of the solar irradiance to compare the solar irradiance transmitted through the composite films. From these results and spectral irradiance of sunlight, a sunlight energy saving ratio was calculated for each day over the wavelength range of 200–1100 nm; the calculated values are given in Table 2. The colored composite films decreased the transmitted solar spectral irradiance by 50% on date B (summer), 36% on date A (spring), and 15% on date C (winter). These results indicate that the composite films in the present investigation automatically adjusted their transmittance depending on the changing sunlight irradiance in each season. Furthermore, the result in Figure 3 demonstrates that the coloring degree on date B (summer) was unsaturated. This suggests that the film could show a more colored state with further sunlight irradiation, and the more colored film would cause more of a decrease in sunlight transmission.

Table 2. Radiant intensity of incident sunlight, intensity transmitted through the bleached and colored composite films, and their energy saving ratios on dates A, B, and C.

Date	A (spring)	B (summer)	C (winter)
Radiant intensity of sunlight	710	921	413
Radiant intensity before coloring (W/m ²)	639	828	371
Radiant intensity after coloring (W/m ²)	409	416	317
Energy saving ratio	36%	50%	15%

For the composite films studied in the present investigation, coloration took more than 1 h in spring and summer, and the bleaching took over 20 h, which is close to one day. In our previous investigations, the coloring time could be accelerated by adding copper or phosphorus to the WO_3 -based composite film (Miyazaki et al., 2012; Miyazaki et al., 2014) and the bleaching time could be shortened by adding phosphorus or reducing the film thickness (Miyazaki et al., 2014; Miyazaki et al., 2015). The coloring and bleaching times of the composite films can be controlled for various purposes; hence, the WO_3 -based composite films studied here can be applied in smart windows, UV sensors, optical memory, etc.

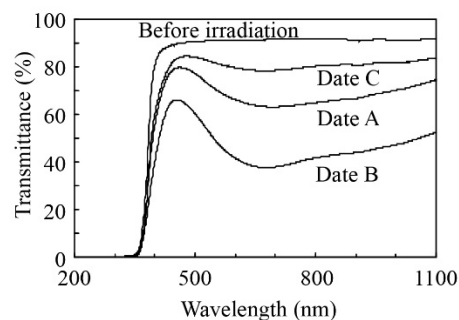


Figure 1. UV-Vis transmittance spectra of the composite films before and after sunlight irradiation (1 h) on dates A, B, and C.

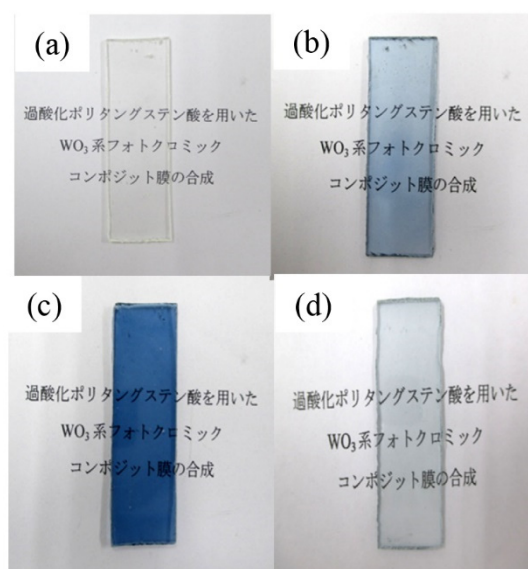


Figure 2. Images of the composite films colored on dates A, B, and C.

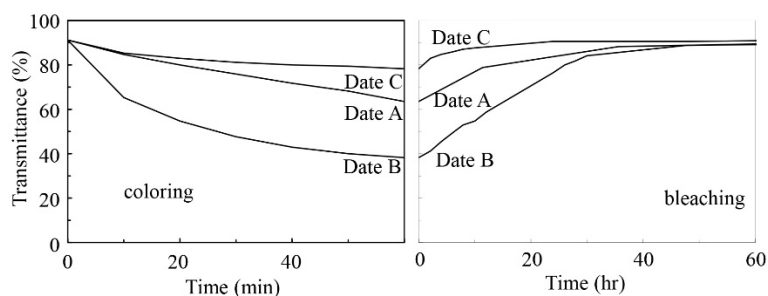


Figure 3. Time dependences of transmittance changes during (a) coloring and (b) bleaching for all composite films.

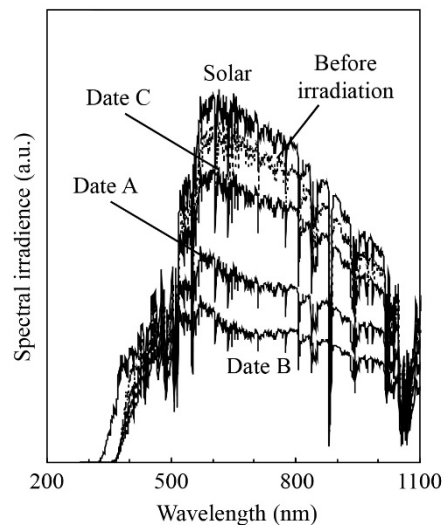


Figure 4. Solar energy reference spectrum and calculated solar energy spectra transmitted through the colored composite films colored on dates A, B, and C.

4. Conclusion

The photochromic properties of WO₃-based composite films were evaluated under sunlight from three seasons (spring, summer, and winter), and the composite films exhibited photochromism induced via sunlight irradiation. The coloring degree of the composite films automatically varied with sunlight radiant intensity, which depends on the season. In conclusion, the WO₃-based composite films fabricated here can be applied as smart windows.

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